CASE WESTERN RESERVE UNIVERSITY EST. 1826

Office of Research Administration
10900 Euclid Avenue
Cleveland, Ohio 44106-7037
phone 216.368.5939
fax 216.368.4679

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Defense Technical Information Center
8725 John J Kingman Road, Sute 0944
Fort Belvoir, VA 22060-6218

To Whom it May Concern:

Please find enclosed the Final Technical Report and SF 298 for N000014-13-1-0691 for your records. Feel free to contact me directly should you need anything further during the closeout process of this award.

Sincerely,

Karen Dunn
Assistant Director, Pre-award Services

Final Report NOOO14-13-1-0691

We conducted a systematic study on the effect of surface roughness on the efficacy of acetylene-based (C_2H_2) carburizing of 316L austenitic stainless steel. Seven types of specimens were prepared: one as-machined and six polished to varying smoothness using the following final polishing media: P400, P800, P1500, and P2500 SiC grit paper; and 3 micron and 1 micron diamond suspension. As expected, the as-machined surface is the roughest, and the roughness decreases with increasing smoothness of the final polish.

All of the specimens were treated with the same acetylene-based carburizing recipe: 16 h at 450 °C in 0.05 liters/minute (lpm) C_2H_2 / 1 lpm H_2 / 5 lpm N_2. The as-machined sample and the sample finished to P400 grit showed only discrete droplet-shaped carburized regions. The sample finished to P800 grit showed a higher density of droplets with more of the surface area covered. However, the carburized surface layer (the "case") is still very thin and not continuous. On the other hand, the finer grit papers (P1500 and P2500) polished samples showed continuous cases. These results clearly demonstrate that acetylene activation is strongly dependent on surface preparation, and that a gaseous hydrochloric (HCl) activation pretreatment is not essential for successful carburization.

X-ray diffractometry (XRD) was used to characterize the surface structure of carburized materials with different surface finishes. The non-treated 316L material shows strong (111) and (200) peaks clearly resolved, as expected. Surface finishing had a substantial influence on acetylene activation and carburization. XRD spectra obtained from the carburized samples finished using coarse grit (P400, P800) samples showed no change in the peak positions of the (111) and (200) peaks, indicating that a negligible amount of carbon had diffused into the samples. Samples polished by the finer SiC grit papers (P1500, P2500) showed peak shifts toward smaller 2 theta angles, which indicates the lattice parameters of these two samples have been expanded by interstitial carbon. The diamond suspension-polished samples have larger peak shifts than the P1500 grit and P2500 grit samples, indicating that these samples have taken up more carbon during the treatment, and therefore have larger lattice parameters. The peak shifts of carburized samples are consistent with the metallographic results.

We used transmission electron microscopy (TEM) to determine the origin of the dramatic surface roughness effect just described. A cross-sectional TEM image obtained from the specimen with a P400 grit surface finish revealed a continuous layer of nano-crystals across the entire specimen surface. There is a layer within 200 nm of the surface, consisting of numerous nano-crystals, whose size varies from 10 nm to nearly 100 nm. The crystals at the external surface are essentially equiaxed and have diameters around 10 nm. The crystals located around 200 nm deeper into the sample are around 100 nm in length and a few tens of nm in width. Compared to the 400 grit sample, the disturbed layer on the 1 micron diamond specimen is much thinner. The crystals are about 100-200 nm long and a few tens of nm in width. The morphology of these crystals on the 1 μm diamond surface resembles the relatively larger nano-crystals located a few hundred nm deeper into the specimen, close to the boundary

between the nano-crystalline layer and transition layer of the P400 grit sample. Clearly, the nano-crystalline layer induced by mechanical deformation during coarse polishing inhibits acetylene-based activation and carburization.

Our next effort involved nitriding experiments on 316L samples carried out at different temperatures from 350 °C to 450 °C. In each process, the nitrogen activity in the gas atmosphere, $a(N_2)$, was fixed at 7400, the nitriding time was fixed at 20 h, and an *in situ* gaseous HCl pre-nitriding activation at 325 °C was included. The nitrogen concentration depth profiles were determined by scanning Auger electron spectroscopy (AES). The nitrogen-rich case depth was strongly dependent on temperature, increasing from ~1 micron to ~15 microns as the nitriding temperature was increased from 350 °C to 450 °C. This results from the strong temperature dependence on nitrogen diffusivity in austenite.

The data also revealed that the surface concentration of nitrogen increases slightly as temperature increases. This is unexpected, inasmuch as the solubility of nitrogen in 316L stainless steel decreases with increasing temperature. We conclude that the incorporation of nitrogen atoms into the 316L lattice is not immediate, but it is contingent on a temperature-dependent process. This is supported by data which reveals that the surface concentration of nitrogen increases slightly with increasing time. We presume that the process of breaking the NH_3 molecules into atomic nitrogen and H_2 molecules, and then incorporating the nitrogen atoms in the 316L lattice, involves both time and thermal energy. Therefore, nitriding at higher temperatures achieves the maximum solubility of nitrogen much more quickly, and produces both a deeper case depth and a higher surface concentration.

The relative brittleness of the hardened "case" on nitrided and nitro-carburized 316L samples was investigated using 10 Newton (1kg) Vickers micro-hardness indentations. At these high loads, readily visible micro-cracks were found on the periphery of the indents on the nitrided samples but not on indents on the nitro-carburized samples (cracking was not observed on indents made with smaller loads, or on carburized samples). This absence of micro-cracking is particularly interesting, given the higher hardness of the nitro-carburized samples (the presence of such micro-cracks, which might arise in service, would be inimical to high cycle fatigue resistance.) The absence of such micro-cracking on the nitro-carburized samples is attributed to the high strength of the carbon-rich region below the nitrogen-rich region at the near-surface regions of these samples.

Because of the heavy machining and subsequent microstructural damage required to create the threads of Navy fasteners, there was concern that such fasteners would have non-continuous hardened corrosion-resistance cases after interstitial hardening. This was investigated using fasteners of the A286 precipitation-hardened stainless steel. Gratifyingly, continuous hardened cases were found after acetylene-based carburization at 440 °C.

Most of these these findings have been reported in top-ranked archival technical journals.

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CASE WESTERN RESERVE UNIVERSITY
10900 EUCLID AVE.
CLEVELAND, OHIO 44106-7015

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9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
NAVAL RESEARCH LABORATORY
Attn. CODE 5596
4555 OVERLOOK AVE. SW
WASHINGTON, DC 20375

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14. ABSTRACT
This program supported the early phases of a Future Naval Capabilities (FNC) program at the Naval Research Laboratory (NRL), devoted to transitioning a novel low temperature (<500 Celsius) interstitial hardening process for stainless steels for impellers, fasteners and other marine items. Although the FNC program is a five (5) year program, CWRU support under this program was available only for the first two (2) years of the FNC program. The objectives of the CWRU effort were to increase the understanding and applications of this exciting technology, focusing on four areas: 1) acetylene-based carburizing, 2) gas phase nitriding, 3) gas phase nitrocarburizing, and 4) carburizing machined fasteners.

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